Supporting information for

Microwave-assisted deep eutectic solvent extraction coupled with headspace solid−phase microextraction followed by GC-MS for analysis of volatile compounds from tobacco

Jing Nie[a], Guowei Yu[a], Zhiyu Song [a], Xiajun Wang[a], Zuguang Li[a,*] Yuanbin She, Mawrong Lee[b]

[a.] *College of Chemical Engineering, Zhejiang University of Technology, Hangzhou 310014, China.*
[b.] *Department of Chemistry, National Chung-Hsing University, Taichung 40227, Taiwan.*

[*] *corresponding author*

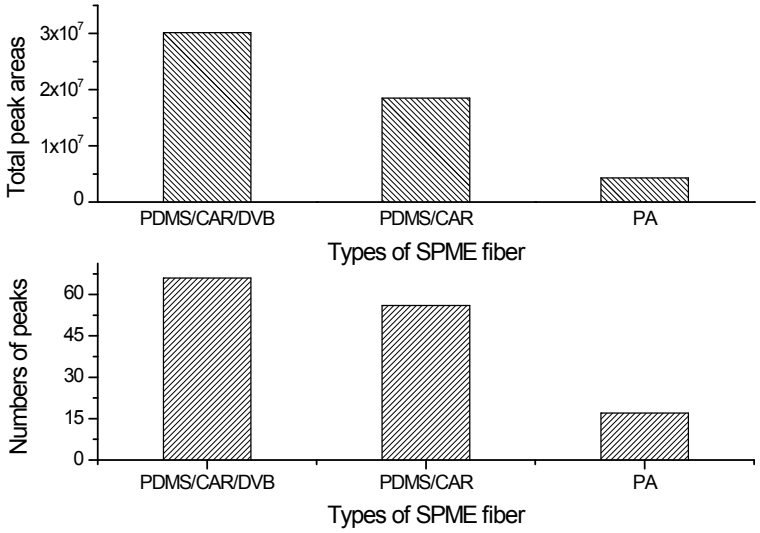

Fig. S1 Effect of types of SPME fiber. Extraction conditions are followed: solvent, DES-2; microwave power, 300 W; set-up temperature, 75 °C; irradiation time, 60 s.

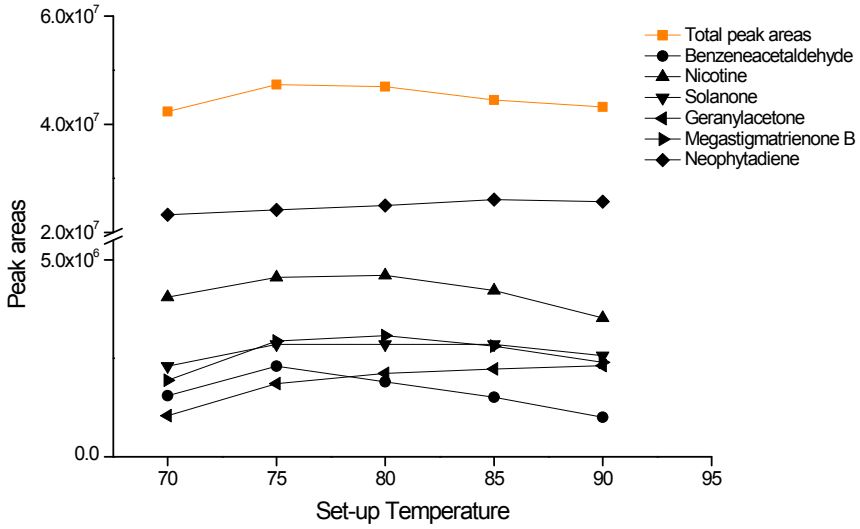

Fig. S2 Effect of set-up temperature. Extraction conditions are followed: fibre, PDMS/DVB/CAR, 50/30 um; solvent, DES-2; microwave power, 500 W; irradiation time, 60 s.

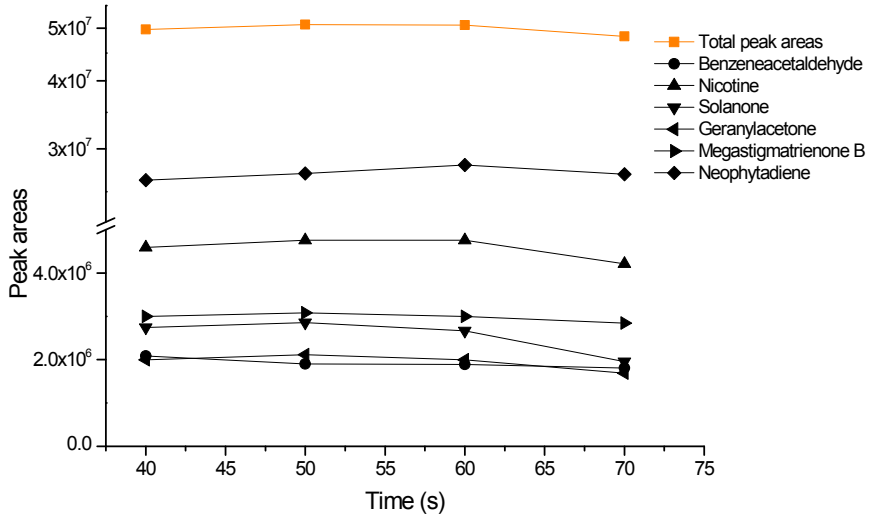

Fig.S3 Effect of irradiation time. Extraction conditions are followed: fibre, PDMS/DVB/CAR, 50/30 um; solvent, DES-2; microwave power, 500 W; set-up temperature, 80 °C.

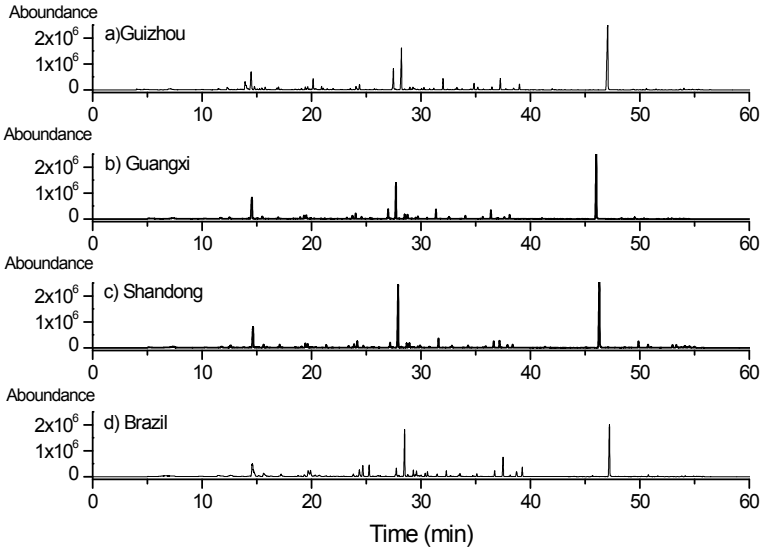

Fig.S4 The total ion chromatograms of volatile compounds in tobacco from different regions

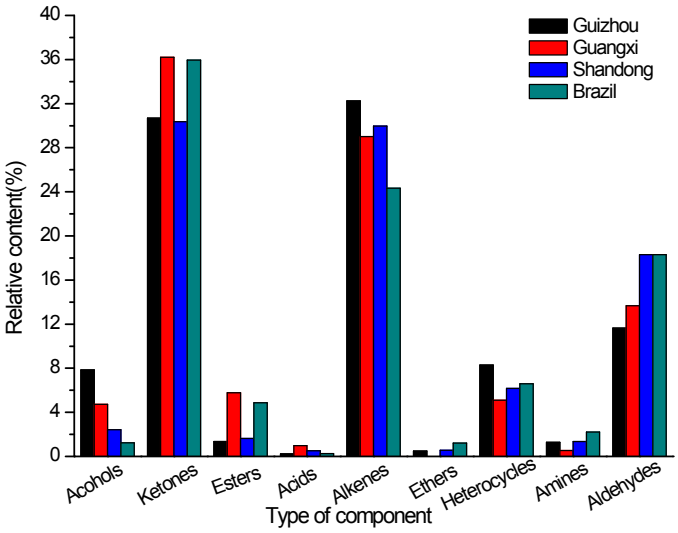

Fig.S5 The relative contents of compounds in tobacco from different regions

Table S1. The volatile components in tobacco obtained by MADESE-SPME, MAE-SPME and SPME

Retention time (min)	Compounds	Formula	Molecular weight	RI[a] (RI[b])	Identification[c]	Relative content (%)		
						MADESE-SPME	MAE-SPME	SPME
12.44	6-Methyl-5-hepten-2-one	$C_8H_{14}O$	120	980(984)	RI, MS	1.20	2.78	--
13.37	Hexyl acetate	$C_8H_{16}O_2$	144	1007(1008)	RI, MS	0.18	0.68	--
13.81	1-Isopropyl-2-methylbenzene	$C_{10}H_{14}$	134	1019(1019)	RI, MS	0.15	--	--
13.92	*o*-Cymene	$C_{10}H_{14}$	134	1022(1021)	RI, MS	--	0.57	--
14.01	Limonene	$C_{10}H_{16}$	136	1024(1026)	RI, MS	2.23	19.58	--
14.20	Benzyl Alcohol	C_7H_8O	108	1031(1032)	RI, MS	2.12	1.32	1.56
14.53	Benzeneacetaldehyde	C_8H_8O	120	1038(1040)	RI, MS	7.92	0.63	0.11
14.83	*p*-Menth-4(8)-ene	$C_{10}H_{18}$	138	1046(1041)	RI, MS	1.09	2.51	0.12
15.11	τ-Terpinene	$C_{10}H_{16}$	136	1053(1055)	RI, MS	0.40	0.52	0.11
15.48	*m*-Tolualdehyde	C_8H_8O	120	1063	MS	0.65	0.47	--
15.79	*N*-methyl-Aniline	C_7H_9N	107	1071(1069)	RI, MS	0.80	1.88	--
16.82	Linalol	$C_{10}H_{18}O$	154	1098(1098)	RI, MS	0.81	1.13	0.23
16.95	(*Z*)-6-Nonenal	$C_9H_{16}O$	140	1098(1101)	RI, MS	0.80	0.61	--
17.17	2-Phenylaziridine	C_8H_9N	119	1107	MS	0.24	--	--
17.91	Phenylethyl alcohol	$C_8H_{10}O$	122	1124(1121)	RI, MS	0.08	0.2	0.56
18.70	Camphor	$C_{10}H_{16}O$	152	1143(1143)	RI, MS	0.15	0.13	0.10
18.95	2-Phenylpropenal	C_9H_8O	132	1149(1148)	RI, MS	0.43	--	--
19.31	3-Ethyl-benzaldehyde	$C_9H_{10}O$	134	1158(1161)	RI, MS	0.71	--	--
19.36	Benzyl acetate	$C_9H_{10}O_2$	150	1159(1161)	RI, MS	--	0.19	--

19.52	1,4-Benzodioxan	$C_8H_8O_2$	136	1163(1164)	RI, MS	0.64	--	--
19.74	2,4-Dimethyl-benzaldehyde	$C_9H_{10}O$	134	1168	MS	--	0.44	--
19.66	Berbenol	$C_{10}H_{16}O$	152	1166(1161)	RI, MS	0.14	--	--
19.81	2,6-Dimethylbenzaldehyde	$C_9H_{10}O$	134	1170	MS	0.15	--	--
20.01	Menthol	$C_{10}H_{20}O$	156	1175(1171)	RI, MS	3.05	6.86	0.10
20.20	Naphthalene	$C_{10}H_8$	128	1186(1189)	RI, MS	0.06	--	--
20.72	α-Terpineol	$C_{10}H_{18}O$	154	1192(1189)	RI, MS	0.84	1.31	0.12
20.86	2,6,6-Trimethyl-1,3-cyclohexadiene-1-carboxaldehyde	$C_{10}H_{14}O$	154	1195(1200)	RI, MS	0.40	0.71	--
21.20	Myrtenal	$C_{10}H_{14}O$	154	1203(1201)	RI, MS	0.24	0.4	0.12
21.71	β-Cyclocitral	$C_{10}H_{16}O$	152	1215(1219)	RI, MS	0.35	0.94	0.11
22.39	Methyl thymyl ether	$C_{11}H_{16}O$	164	1231(1235)	RI, MS	0.10	0.28	0.10
22.48	2-Methylbutyricacid hexyl ester	$C_{11}H_{22}O_2$	186	1233(1236)	RI, MS	0.23	--	--
23.23	*p*-Formylanisole	$C_8H_8O_2$	136	1249(1245)	RI, MS	0.40	--	--
23.75	2-methoxy-4-methyl-benzenamine	$C_8H_{11}NO$	137	1263(1294)	RI, MS	1.27	--	--
24.04	Butoxy-benzene	$C_{10}H_{14}O$	150	1270	MS	1.59	--	--
24.57	Bornyl acetate	$C_{10}H_{12}O$	148	1283(1287)	RI, MS	0.09	0.12	0.14
25.37	2-(Phenylmethyl)-1,3-dioxolane	$C_{10}H_{12}O_2$	164	1301	MS	0.37	--	--
25.54	Cuminic alcohol	$C_{10}H_{14}O$	150	1305(1305)	RI, MS	0.17	--	--
27.02	Nicotine	$C_{10}H_{14}N_2$	162	1340(1344)	RI, MS	6.24	3.97	31.79
27.23	α-Ionene	$C_{13}H_{18}$	174	1346(1349)	RI,MS	0.13	--	--
27.75	Solanone	$C_{13}H_{22}O$	194	1358(1360)	RI, MS	13.06	11.84	1.97
28.02	5,5-Dimethyl-3-propenyl-2-cyclohexen-1-one	$C_{11}H_{16}O$	164	1363	MS	0.20	0.18	0.18
28.34	Ylangene	$C_{15}H_{24}$	204	1370(1374)	RI, MS	--	--	0.91
28.52	1-(2,6,6-Trimethyl-1,3-cyclohexadien-1-yl)-2-buten-1-one	$C_{13}H_{18}O$	190	1375(1373)	RI, MS	0.65	0.95	0.13

28.78	α-Damascenone	$C_{13}H_{18}O$	190	1381(1378)	RI, MS	1.36	0.54	0.13
29.73	β-Damascone	$C_{13}H_{20}O$	192	1403(1402)	RI, MS	0.55	0.83	1.51
30.23	α-Santalene	$C_{15}H_{24}$	204	1416(1417)	RI, MS	0.19	0.21	0.29
30.57	Methyl 9-oxodecanoate	$C_{11}H_{20}O_3$	200	1424(1429)	RI, MS	0.44	--	
31.38	Geranylacetone	$C_{13}H_{22}O$	194	1444(1445)	RI, MS	2.91	2.98	1.87
32.58	β-Ionone	$C_{13}H_{20}O$	192	1473(1470)	RI, MS	0.48	0.39	0.85
32.82	Nicotyrine	$C_{10}H_{10}N_2$	158	1478	MS	--	--	1.21
33.04	β-Eudesmene	$C_{15}H_{24}$	204	1485(1486)	RI, MS	0.28	0.1	--
33.10	β-Himachalene	$C_{15}H_{24}$	204	1490(1495)	RI, MS	--	0.13	--
33.82	4-(5,5-Dimethyl-1-oxaspiro[2.5]oct-4-yl)-3-buten-2-one	$C_{13}H_{22}O_2$	210	1504(1501)	RI, MS	0.32	--	--
33.88	α-Farnesene	$C_{15}H_{24}$	204	1506(1508)	RI, MS	--	0.15	--
34.08	Octahydro-4a-methyl-1,5-naphthalenedione	$C_{11}H_{16}O_2$	180	1511	MS	1.84	1.09	--
34.39	Spiro[5.6]dodecan-7-one	$C_{12}H_{20}O$	180	1519(1524)	RI, MS	0.76	0.53	1.11
34.67	4,5,7,7a-Tetrahydro-4,4,7a-trimethyl-2(6H)benzofuranone	$C_{11}H_{16}O_2$	180	1526(1528)	RI, MS	--	--	0.83
34.89	Nerolidol	$C_{15}H_{26}O$	222	1532(1533)	RI, MS	0.20	0.17	--
35.66	Megastigmatrienone A	$C_{13}H_{18}O$	190	1551(1555)	RI, MS	0.82	0.53	0.35
36.41	Megastigmatrienone B	$C_{13}H_{18}O$	190	1571(1573)	RI, MS	3.33	1.87	1.05
36.92	Bisisobutyric acid 1-tert-butyl-2-methylpropane-1,3-diyl ester	$C_{16}H_{30}O_4$	286	1584	MS	0.26	0.26	--
37.61	Megastigmatrienone C	$C_{13}H_{18}O$	190	1602(1604)	RI, MS	0.56	0.4	0.41
38.12	Megastigmatrienone D	$C_{13}H_{18}O$	190	1615(1617)	RI, MS	1.60	0.85	0.67
44.96	Solavetivone	$C_{15}H_{22}O$	218	1798(1796)	RI, MS	0.32	0.27	0.29
46.07	Neophytadiene	$C_{20}H_{38}$	278	1833(1836)	RI, MS	25.56	21.06	46.18
47.81	3,7,11,15-Tetramethyl-2-hexadecen-1-ol	$C_{20}H_{40}O$	296	1878(1882)	RI, MS	--	--	0.39

48.93	*n*-Hexadecanoic acid methyl ester	$C_{17}H_{34}O_2$	270	1923(1924)	RI, MS	--	0.09	--
48.99	Farnesyl acetone	$C_{18}H_{30}O$	262	1925(1927)	RI, MS	0.21	0.23	0.32
49.54	2,2'-(1,2-Ethanediyl)bis[6,6-dimethyl-bicyclo[3.1.1]hept-2-ene	$C_{20}H_{30}$	270	1942	MS	0.37	--	--
50.39	*n*-Hexadecanoic acid	$C_{16}H_{32}O_2$	256	1969(1966)	RI, MS	0.24	--	--
52.59	Thunbergol	$C_{20}H_{34}O$	290	2039(2040)	RI, MS	0.25	--	--
52.91	3,7,11,15-Tetramethylhexadeca-1,6,10,14-tetraen-3-ol	$C_{20}H_{34}O$	290	2049(2050)	RI, MS	0.40	--	--
53.35	Methyl 2,5-octadecadiynoate	$C_{19}H_{30}O_2$	290	2063	MS	0.15	--	--
53.66	2-[2-(6,6-Dimethylbicyclo[3.1.1]hept-2-en-2-yl)ethyl]-6,6-dimethylbicyclo[3.1.1]hept-2-ene	$C_{20}H_{30}$	270	2073	MS	0.19	--	--
54.69	4,8,13-Duvatriene-1,3-diol	$C_{20}H_{34}O2$	306	2107(2109)	RI, MS	0.04	--	--

a) RI^a —Calculation retention index based on the DB-5ms or DB-5 column;

b) RI^b — Retention index in the literature;

c) -- — Not founded.

Table S2. The volatile components in different areas of tobacco

Retention time (min)	Compounds	Formula	RI[a] (RI[b])	Identification[c]	Relative content (%)			
					Guizhou	Guangxi	Shandong	Brzail
12.44	6-Methyl-5-hepten-2-one	$C_8H_{14}O$	980(984)	RI, MS	1.20	1.32	1.10	--
13.37	Hexyl acetate	$C_8H_{16}O_2$	1007(1008)	RI, MS	0.18	0.11	0.20	0.10
13.81	1-Isopropyl-2-methylbenzene	$C_{10}H_{14}$	1019(1019)	RI, MS	0.15	--	--	--
14.01	Limonene	$C_{10}H_{16}$	1024(1026)	RI, MS	2.23	1.01	--	--
14.20	Benzyl Alcohol	C_7H_8O	1031(1032)	RI, MS	2.12	--	0.35	--
14.53	Benzeneacetaldehyde	C_8H_8O	1038(1040)	RI, MS	7.92	10.26	13.86	10.23
14.84	*p*-Menth-4(8)-ene	$C_{10}H_{18}$	1046(1041)	RI, MS	1.09	--	--	--
15.10	τ-Terpinene	$C_{10}H_{16}$	1053(1055)	RI, MS	0.40	0.30	0.35	0.50
15.48	*m*-Tolualdehyde	C_8H_8O	1063	MS	0.65	--	1.14	2.40
15.79	*N*-methyl-Aniline	C_7H_9N	1071(1069)	RI, MS	0.80	0.56	0.42	0.13
16.82	Linalol	$C_{10}H_{18}O$	1098(1098)	RI, MS	0.81	1.14	0.67	0.55
16.95	(*Z*)-6-Nonenal	$C_9H_{16}O$	1098(1101)	RI, MS	0.80	0.71	0.64	0.84
17.17	2-Phenylaziridine	C_8H_9N	1107	MS	0.24	0.90	0.19	--
17.91	Phenylethyl alcohol	$C_8H_{10}O$	1124(1121)	RI, MS	0.08	0.20	0.56	--
18.69	Camphor	$C_{10}H_{16}O$	1143(1143)	RI, MS	0.15	0.18	--	--
18.96	2-Phenylpropenal	C_9H_8O	1149(1148)	RI, MS	0.43	0.47	0.72	0.87
19.31	3-Ethyl-benzaldehyde	$C_9H_{10}O$	1158(1161)	RI, MS	0.71	1.25	1.22	3.51

19.52	1,4-Benzodioxan	$C_8H_8O_2$	1163(1164)	RI, MS	0.64	1.45	1.00	2.78
19.66	Berbenol	$C_{10}H_{16}O$	1166(1161)	RI, MS	0.14	--	--	--
19.81	2,6-Dimethylbenzaldehyde	$C_9H_{10}O$	1170	MS	0.15	0.17	0.21	0.33
20.01	Menthol	$C_{10}H_{20}O$	1175(1171)	RI, MS	3.05	--	--	--
20.20	Naphthalene	$C_{10}H_8$	1186(1189)	RI, MS	0.06	0.30	0.09	--
20.72	α-Terpineol	$C_{10}H_{18}O$	1192(1189)	RI, MS	0.84	1.31	--	
20.86	2,6,6-Trimethyl-1,3-cyclohexadiene-1-carboxaldehyde	$C_{10}H_{14}O$	1195(1200)	RI, MS	0.40	0.11	0.15	0.12
21.20	Myrtenal	$C_{10}H_{14}O$	1203(1201)	RI, MS	0.24	0.68	0.23	--
21.71	β-Cyclocitral	$C_{10}H_{16}O$	1215(1219)	RI, MS	0.35	--	0.13	--
22.39	Methyl thymyl ether	$C_{11}H_{16}O$	1231(1235)	RI, MS	0.10	--	--	0.20
22.49	2-Methylbutyricacid hexyl ester	$C_{11}H_{22}O_2$	1233(1236)	RI, MS	0.23	--	--	--
23.23	*p*-Formylanisole	$C_8H_8O_2$	1249(1245)	RI, MS	0.40	--	0.55	1.02
23.75	2-methoxy-4-methyl-benzenamine	$C_8H_{11}NO$	1263(1294)	RI, MS	1.27	0.54	1.35	2.21
24.04	Butoxy-benzene	$C_{10}H_{14}O$	1270	MS	1.59	1.28	2.11	3.85
24.57	Bornyl acetate	$C_{10}H_{12}O$	1283(1287)	RI, MS	0.09	1.96	0.57	3.38
25.37	2-(Phenylmethyl)-1,3-dioxolane	$C_{10}H_{12}O_2$	1301	MS	0.37	0.57	0.46	0.46
25.54	Cuminic alcohol	$C_{10}H_{14}O$	1305(1305)	RI, MS	0.17	0.18	--	0.28
27.02	Nicotine	$C_{10}H_{14}N_2$	1340(1344)	RI, MS	6.24	1.63	4.11	3.23
27.23	α-Ionene	$C_{13}H_{18}$	1346(1349)	RI,MS	0.13	0.15	0.19	0.28
27.75	Solanone	$C_{13}H_{22}O$	1358(1360)	RI, MS	13.06	22.69	14.72	15.32
28.02	5,5-Dimethyl-3-propenyl-2-cyclohexen-1-one	$C_{11}H_{16}O$	1363	MS	0.20	--	0.27	0.55
28.52	1-(2,6,6-Trimethyl-1,3-cyclohexadien-1-yl)-2-buten-1-one	$C_{13}H_{18}O$	1375(1373)	RI, MS	0.65	1.20	1.47	1.64
28.78	α-Damascenone	$C_{13}H_{18}O$	1381(1378)	RI, MS	1.36	0.45	1.29	1.33

29.21	1-Mesityl-1,3-butadiene	$C_{13}H_{16}$	1383(1385)	RI, MS	--	--	--	0.50
29.73	β-Damascone	$C_{13}H_{20}O$	1403(1402)	RI, MS	0.55	0.42	0.21	--
30.23	α-Santalene	$C_{15}H_{24}$	1416(1417)	RI, MS	0.19	0.21	0.29	--
30.57	Methyl 9-oxodecanoate	$C_{11}H_{20}O_3$	1424(1429)	RI, MS	0.44	0.61	0.39	0.71
31.38	Geranylacetone	$C_{13}H_{22}O$	1444(1445)	RI, MS	2.91	2.68	3.52	1.57
32.58	β-Ionone	$C_{13}H_{20}O$	1473(1470)	RI, MS	0.48	0.39	0.85	--
33.04	β-Eudesmene	$C_{15}H_{24}$	1485(1486)	RI, MS	0.28	--	--	--
33.82	4-(5,5-Dimethyl-1-oxaspiro[2.5]oct-4-yl)3-buten-2-one,	$C_{13}H_{22}O_2$	1504(1501)	RI, MS	0.32	--	--	--
34.08	Octahydro-4a-methyl-1,5-naphthalenedione	$C_{11}H_{16}O_2$	1511	MS	1.84	0.80	1.18	0.82
34.39	Spiro[5.6]dodecan-7-one	$C_{12}H_{20}O$	1519(1524)	RI, MS	0.76	--	--	--
34.89	Nerolidol	$C_{15}H_{26}O$	1532(1533)	RI, MS	0.20	0.20	--	--
35.66	Megastigmatrienone A	$C_{13}H_{18}O$	1551(1555)	RI, MS	0.82	0.51	0.35	1.74
36.41	Megastigmatrienone B	$C_{13}H_{18}O$	1571(1573)	RI, MS	3.33	1.98	1.98	5.85
36.92	Bisisobutyric acid 1-tert-butyl-2-methylpropane-1,3-diyl ester	$C_{16}H_{30}O_4$	1584(1589)	RI, MS	0.26	2.01	0.16	0.57
37.61	Megastigmatrienone C	$C_{13}H_{18}O$	1602(1604)	RI, MS	0.56	1.07	0.88	2.00
38.12	Megastigmatrienone D	$C_{13}H_{18}O$	1615(1617)	RI, MS	1.60	0.94	1.63	2.89
44.96	Solavetivone	$C_{15}H_{22}O$	1798(1796)	RI, MS	0.32	0.34	0.30	1.19
46.07	Neophytadiene	$C_{20}H_{38}$	1833(1836)	RI, MS	25.56	22.91	26.56	18.37
49.00	Farnesyl acetone	$C_{18}H_{30}O$	1925(1927)	RI, MS	0.21	0.11	0.12	0.14
49.54	2,2'-(1,2-Ethanediyl)bis[6,6-dimethyl-bicyclo[3.1.1]hept-2-ene	$C_{20}H_{30}$	1942	MS	0.37	2.00	0.11	0.61
50.39	*n*-Hexadecanoic acid	$C_{16}H_{32}O_2$	1969(1966)	RI, MS	0.24	0.97	0.52	0.25
52.59	Thunbergol	$C_{20}H_{34}O$	2039(2040)	RI, MS	0.25	1.00	0.66	0.26

52.91	3,7,11,15-Tetramethylhexadeca-1,6,10,14-tetraen-3-ol	$C_{20}H_{34}O$	2049(2050)	RI, MS	0.40	1.08	0.26	0.27
53.35	Methyl 2,5-octadecadiynoate	$C_{19}H_{30}O_2$	2063	MS	0.15	0.32	--	--
53.66	2-[2-(6,6-Dimethylbicyclo[3.1.1]hept-2-en-2-yl)ethyl]-6,6-dimethylbicyclo[3.1.1]hept-2-ene	$C_{20}H_{30}$	2073	MS	0.19	0.82	0.25	0.2
53.97	Methyl linolelaidate	$C_{19}H_{34}O_2$	2103(2102)	RI, MS	--	0.76	0.29	0.09
54.69	4,8,13-Duvatriene-1,3-diol	$C_{20}H_{34}O_2$	2107(2109)	RI, MS	0.04	0.38	0.18	0.13

a) RI^a —Calculation retention index based on the DB-5ms or DB-5 column;

b) RI^b — Retention index in the literature;

c) -- — Not founded.